DISCUSSION ON THE COMPOSITION AND TRANSPORT COEFFICIENTS CALCULATION MADE IN PLASMA OUT OF EQUILIBRIUM

Pascal André, Jacques Aubreton, Mario da Silva, Michel Dudeck, Marie-Françoise Elchinger, Bruno Lopez

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P. Andre[1], J. Aubreton[2], M. Lino Da Silva [3], M. Dudeck[4], M.F. Elchinger[2], B. Lopez[3]

[1] Clermont Université, Université Blaise Pascal, LAEPT, BP 10448, F-63000 Clermont Ferrand
[2] SPCTS, Université de Limoges, SPCTS, Centre Européen de la Céramique, 12 Rue Atlantis, 87068 Limoges cedex
[3] Instituto de Plasmas e Fusao Nuclear, Laboratorio Associado, Instituto Superior , Tecnico Av. Rovisco Pais, 1049-001, Lisboa, Portugal
[4] Institut Jean Le Rond d'Alembert, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris cedex, France

ABSTRACTS

In this paper, the composition calculation in plasma out of thermal equilibrium is discussed and we test the viscosity formulations of Wilke, Gupta et al, Chapman Enskog and Sutherland in air plasma out of thermal equilibrium. Finally we applied the formulations to Fire II reentry.

1. INTRODUCTION

In a first step from the H theorem we discuss the composition obtaining in plasma out of thermal equilibrium. We apply the method to the air plasma. In a second step we discuss the viscosity formulation given by Wilke [1], Gupta et al [2], Sutherland [3] and by Chapman Enskog [4]. Finally we apply them to stagnation line of FIRE II reentry (Earth reentry – 1965).

2. COMPOSITION CALCULATION.

The calculation of composition made in plasma out of thermal equilibrium is debatable, several methods can be used as pseudo kinetic method [5], maximization of entropy method [6], Gibbs free energy minimization [7], mass action laws [8, 9], state to state methods [10]. It seems interesting to start both for the composition and for transport coefficients from the same formulation, respectively the Boltzmann equation and the Boltzmann's *H*-theorem. As a matter of fact, taking account that the methods classically used to determine the transport coefficients that is to say Chapman Enskog or Grad methods [11], begin the calculation with the Boltzmann equation [11]:

$$\frac{\partial f_i}{\partial t}+\left(\vec{v}_i.\frac{\partial f_i}{\partial \vec{r}}\right)+\frac{1}{m_i}\left(\vec{X}_i.\frac{\partial f_i}{\partial \vec{v}_i}\right) = \sum_j \iiint \left(f_i^{'} f_j^{'} - f_i f_j\right) g_{ij}\, b\, db\, d\varepsilon\, d\vec{v}_j \qquad (1)$$

where $f_i(\vec{r},\vec{v}_i,t)$ is the distribution function $\vec{X}_i$ is an external force applied on the particle of the i^{th} species, b is the impact parameter, g_{ij} is the initial relative velocity, and ε is the angle over which integration takes place. The resolution of Boltzmann equation by Chapman Enskog, introduce a perturbation function ϕ_i as $f_i = f_i^0(1+\phi_i)$. This latter assume that the external forces is low enough to consider only a small perturbation of the distribution function. Following the Chapman Enskog resolution and taking Sonine polynomials one can obtain integral series depending of integral cross sections [4].

The *H*-theorem, or Boltzmann's *H*-theorem, is a demonstration of the tendency of the particles of an isolated system to approach their equilibrium distribution. The *H*-function for a mixture of species i with distribution functions $f_i(\vec{r},\vec{v}_i,t)$, where $\vec{r}$ is the position, $\vec{v}_i$ is the velocity of species *i*, and *t* is the time, is defined as:

$$H(t) = \sum_i \int\int f_i(\vec{r},\vec{v}_i,t)\ln\left[f_i(\vec{r},\vec{v}_i,t)\right] d\vec{v}_i d\vec{r} \qquad (2)$$

It can be shown that $H=-S_v/k$, where S_v is the entropy per unit volume, and k is Boltzmann's constant. The *H*-function can be viewed as generalization of the entropy, since, unlike entropy defined on a strictly thermodynamic basis, it is defined in non-equilibrium situations. The *H*-theorem states that $dH/dt \le 0$ for an isolated system, and is hence a statement of the second law of thermodynamics it can be deduced that $T_i = T_j$, i.e., that the temperatures of all species are identical. We conclude that, in the absence of external forces, a uniform plasma has only a unique temperature. But by introducing external forces we

can show that the H-function is stable in time $\frac{dH(t)}{dt}=0$. Since the entropy is directly related to the H-function, we can write:

$$\frac{dS}{dt}=\frac{d(\sum_i (S_i^{\text{int}}+S_i^{ext})}{dt}=0 \qquad (3)$$

where S is the entropy of the whole system, S_i^{int} is the entropy related to the distribution function and exchanges between the different species during collisions, and S_i^{ext} is the entropy related to the external forces and gradients. In equilibrium, the entropy of the total system, taking into account external forces and gradients, is stable in time. However, it is not possible to draw any conclusions about the evolution of S_i^{int} or $\sum_i S_i^{\text{int}}$. The calculation shows that minimization of free energy or internal energy is an appropriate method for calculating the composition of a multi-temperature plasma that is stable in time. This result is in accordance with that of Giordano and Capitelli [6].

To use the Chapman Enskog method, we have to assume that the external force is sufficiently low to be considered as a perturbation function and high enough to create a thermal non equilibrium between electrons and heavy species temperature. We have to notice that the latter remarks imply that the plasma is at chemical equilibrium.

So we decided to calculate the composition with the Gibbs free energy method. The first limitation is how to calculate the partition function for diatomic species as a matter of fact the partition function is written as

$$Z_{\text{int}}=\sum_e g_e e^{-hcT_e/kT_{ex}} \sum_v^{v\max} e^{-hcG_e(v)/kT_{vib}} \sum_j^{j\max}(2j+1)e^{-hcF_v(j)/kT_{rot}}$$

where h is Planck constant, c speed of light, T_e the electronic energy of state e, $G_e(v)$ the vibrational energy of the v vibrational level of the electronic state e, $F_v(j)$ the rotational energy of the j rotational level of the vibrational level v. T_{ex}, T_{vib} and T_{rot} are respectively the excitational, vibrational and rotational temperatures. A summation is made on all quantum levels excitational, vibrational and rotational. To determine the chemical potential that is the summation of translational, excitational, vibrational and rotational chemical potential with the foramation enthalpy e^0:

$$\mu^o=\mu^{tr}(T_{tr})+\mu^{ex}(T_{ex})+\mu^{vib}(T_{vib})+\mu^{rot}(T_{rot})+e^o$$

we separate artificially the internal partition function of diatomic species:

$$Z_{\text{int}}=\left(\sum_e g_e e^{-hcT_e/kT_{ex}}\right)\left(\sum_{v=0}^{v\max(1)} e^{-hcG_1(v)/kT_{vib}}\right)\left(\sum_{j=0}^{j\max(0)}(2j+1)e^{-hcF_0(j)/kT_{rot}}\right)$$

We have to notice that some authors propose series development to calculate the internal partition see for example [12] and literature inside.

In the case of plasma out of chemical equilibrium and out of thermal equilibrium the plasma reach a composition at chemical equilibrium but can be out of thermal equilibrium. So we have to consider the external constraints [6] and the hypothesis on the internal temperatures [13]. In figure 1 we show the composition versus time with a model with 34 reactions [14] that reach an air plasma out of thermal equilibrium ($\theta=\frac{T_e}{T_H}=2$) at T_H = 3000 K and at atmospheric pressure for air. The temperatures T_e, T_H are frozen during the time evolution. We have to note that usually the coefficients rates are not known precisely a factor of one thousand can exist between authors so the inverse reaction coefficients rate are estimated with the chemical equilibrium coefficients.

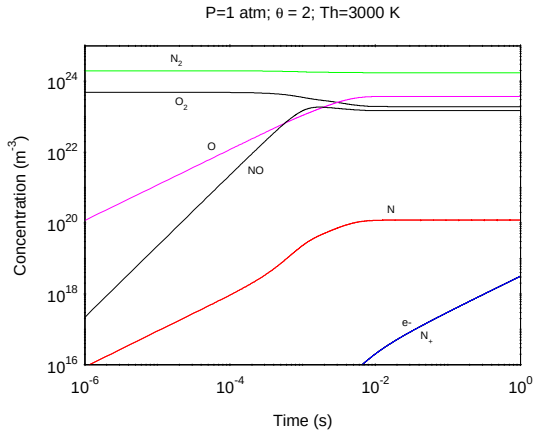

Figure 1: Air Composition versus time

The chemical equilibrium is reach around a time of 10 ms for the main neutral chemical species. However the densities of charged particles continue to increase but with very low concentrations. In the two figures 2 and 3, we represent the composition at chemical equilibrium successively at thermal equilibrium and out of thermal equilibrium obtained by the Gibbs free energy method. Since the energy inside the plasma is higher for a given heavy species temperature the ionization is made at lower temperature. The dissociation is made at lower temperature since the hypothesis on internal temperature is $T_{ex}=T_{vib}=T_{tre-}$ and $T_{rot}=T_H$ the upper quantum energy level of molecules are statistically more populated so the ionization is made at lower heavy species temperature.

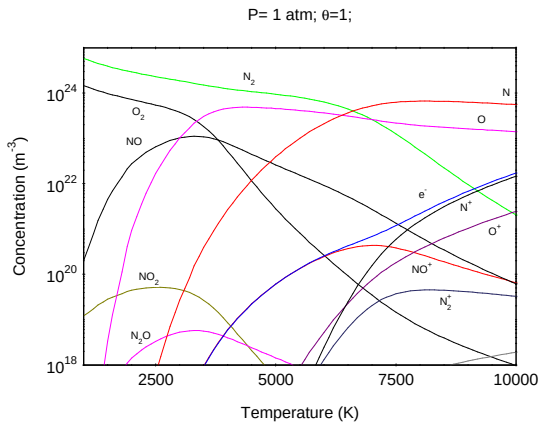

Figure 2. Air Composition at thermal equilibrium

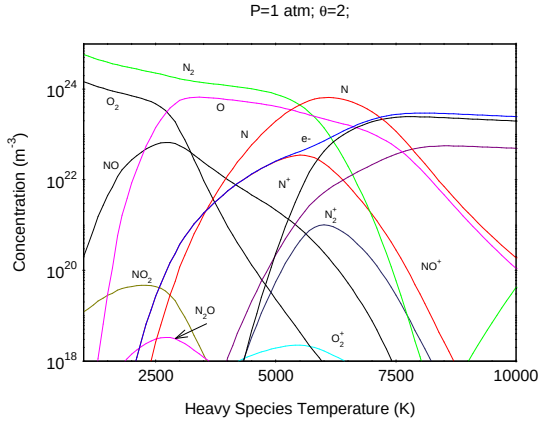

Figure 3. Air composition out of thermal equilibrium

As classic result, the species with a double charge will appear at a greater energy.

3. TRANSPORT COEFFICIENTS.

In a previous work [4] new transport coefficients in plasma out of thermal equilibrium have been developed. In a recent work [15] Colombo and al claim that the results of viscosity are similar between this method and those developed at thermal equilibrium. Taking into account the fact that in plasma modeling it is useful to use fast and quite accurate formulations as those from Wilke [1], Sutherland [3], Gupta and al [2]. It would be interesting to test the formulation used for numerical purpose in the case of plasma out of thermal equilibrium.

The viscosity equation of gas has been given by Wilke in 1950 [1] for a mixture in thermal equilibrium. He proposed a simple and convenient formulation in numerical used. It is used until now:

$$\mu_{Wilke} = \sum_{i=1}^{N} \frac{\mu_i}{1 + \frac{1}{x_i} \sum_{j=1, j\neq i}^{N} x_j \phi_{ij}} \qquad (4)$$

where x_i is the molar fraction of i chemical species, N the number of chemical species taken into account, μ_i is the viscosity of chemical species i given by : $\mu_i = 0.1 \exp\left[\left(A\ln(T) + B\right) + C\right]$

The coefficients A, B and C are Blottner coefficients and be find in several work, we used those given in [16] and report in table 1. The coefficient ϕ_{ij} is given by:

$$\phi_{ij} = \frac{\left[1 + \left(\mu_i / \mu_j\right)^{1/2} \left(M_j / M_i\right)^{1/4}\right]^2}{\left(4/\sqrt{2}\right)\left[1 + \left(M_j / M_i\right)\right]^{1/2}} \qquad (4)$$

where M_i is the molar weight of i chemical species.

Species	A	B	C
N_2	2.68E-02	3.18E-01	-1.13E+01
O_2	4.49E-02	-8.26E-02	-9.20E+00
NO	4.36E-02	-3.36E-02	-9.58E+00
N	1.16E-02	6.03E-01	-1.24E+01
O	2.03E-02	4.29E-01	-1.16E+01
NO^+	3.02E-01	-3.5039791	-3.74E+00
N_2^+	2.68E-02	3.18E-01	-1.13E+01
O_2^+	4.49E-02	-8.26E-02	-9.20E+00
N^+	1.16E-02	6.03E-01	-1.24E+01
O^+	2.03E-02	4.29E-01	-1.16E+01
e^-	0	0	-1.20E+01

Table 1: Blottner coefficients used is this work [16]

The Gupta, Yos, Thompson and Lee approach [2] used the formulation given in [11] for individual viscosity of each chemical species μ_i :

$$\mu_i = \left[\exp\left(C_{\mu_i}\right)\right] T^{\left[A_{\mu_i} \ln(T) + B_{\mu_i}\right]} \qquad (5)$$

where A_{μ_i}, B_{μ_i} and C_{μ_i} are fitting coefficients given in [2]. And finally the total viscosity of the plasma is:

$$\mu_{Gupta\_et\_al} = \sum_{i=1}^{N} x_i \mu_i \qquad (6)$$

At thermal equilibrium, with Chapman Enskog method one can reach more accurate transport coefficients. The interaction potential of each collision has to be known precisely: neutral neutral, charged-charged, charged-neutral, electron-neutral [17, 18]. We have to note that usually a Coulombian shielded potential depending on the Debye length is used for the charged-charged interaction. So, all the interactions between charged particles are identical consequently, we have to find the same viscosity for charged particle. This is not observed in table 1. So we compare the individual viscosity between authors in figure 4 and 5.

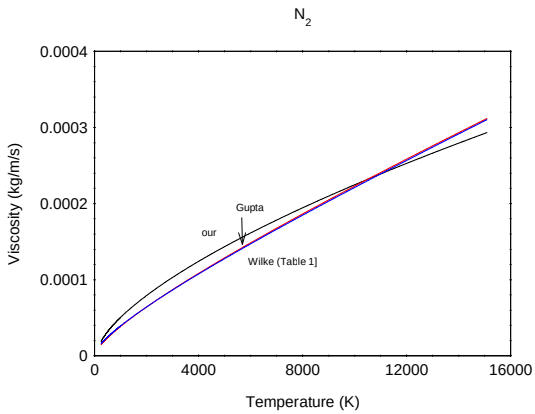

Figure 4. Individual viscosity of diatomic nitrogen N_2.

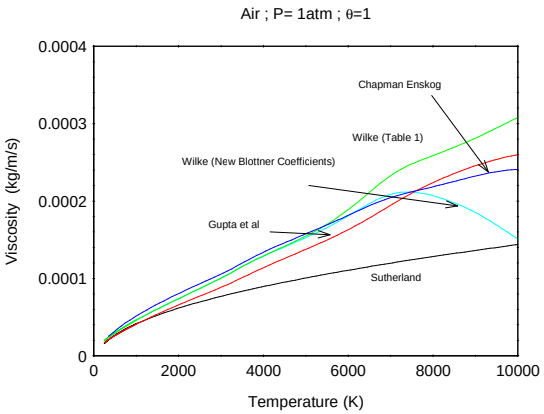

Figure 6. Viscosity at thermal equilibrium

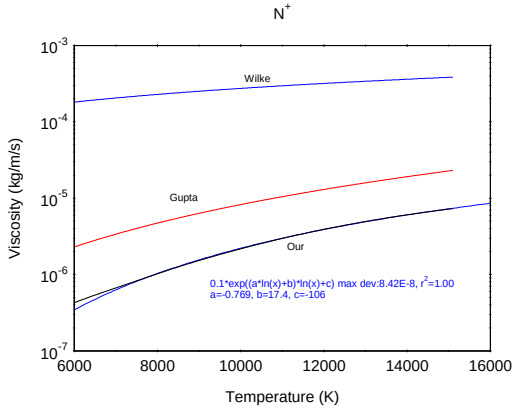

Figure 5. Individual viscosity of nitrogen ions N^+.

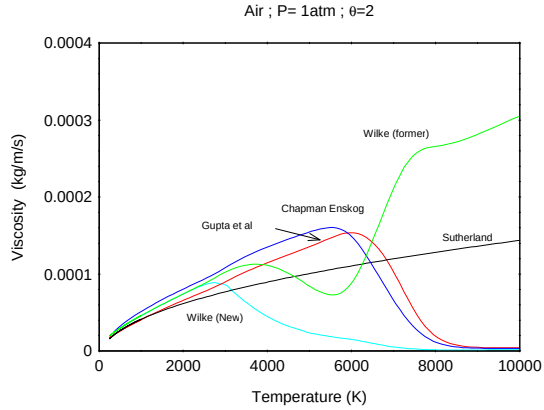

Figure 7. Viscosity out of thermal equilibrium

In figure 4, we show the viscosity for N_2 versus temperature and in figure 5 the viscosity for N^+ versus temperature. For the ions, one can note the large difference of values from Wilke, Gupta and our calculation. Generally, the viscosities of the neutral species are within the same order of magnitude between authors unlike for the ions and electrons. So we propose new Blottner coefficients for charged particles *A=-0.769; B=17.4* and *C=-106* giving a convenient approximation of the results obtained by the Chapman-Enskog method and able to be easily used in numerical codes. The curves with this set of values are indicated as "Wilke (new)".

In figure 6, we have plotted the viscosity at atmospheric pressure and at thermal equilibrium using the various data. In the considered temperature range at thermal equilibrium the results are quiet similar unlike in plasma out of thermal equilibrium represented in figure 7.

At high temperature the behavior of the viscosity is strongly depending of the model (figure 7). The viscosity is continually increasing with the models of Wilke (table 1) and Sutherland when its is decreasing after 6000K for the models of Gupta and Chapman Enskog. By comparing the figure 6 and 7 with figures 4 and 5, we observe that the differences are mainly observed when the ionization is made. Consequently, the errors in viscosities are due to the interaction between ionized particles. As a matter of fact classically the Coulombian interaction depends on the Debye that depends on composition.

The FIRE II mission has been done in May 1965 to analyze the radiation heating during an Earth reentry. In figure 8, we have plotted the composition on the stagnation lines in FIRE II reentry [19]. The viscosity obtained through the stagnation is reported in figure 9. We show large discrepancies between the Wilke formulations using the two set of Blottner coefficients.

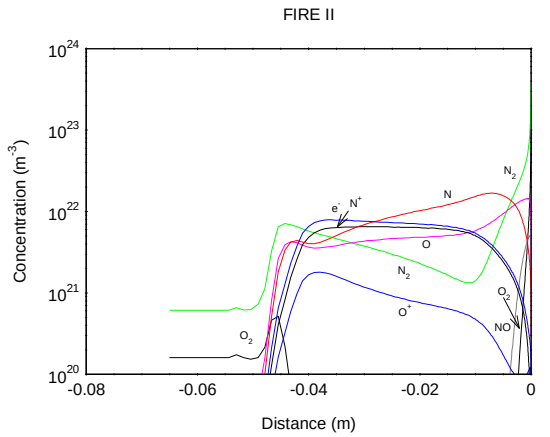

Figure 8. Composition on stagnation line. The stagnation points located at 0.

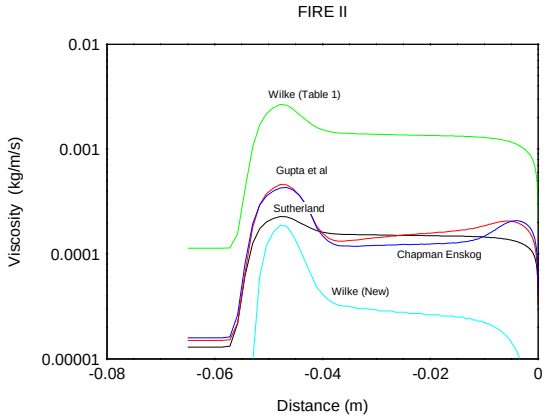

Figure 9. Viscosity on stagnation line at 1634 s (Fire II)

This result suggests that the hydrodynamic models of the plasma flow around the probe could be re-examined with the use of transport coefficients from Chapman-Enskog-Wilke model.

4. CONCLUSION

Through this paper several questions arise: how can we calculate accurately the diatomic partition function in plasma out of equilibrium? What are the influences of non Bolzmann distribution on the transport coefficients? The applied forces have to be high enough to get plasma out of thermal equilibrium but low enough to use the Chapman Enskog method. How can we check the validity of Chapman Enskog approach?

We have shown that the chemical models using chemical rates as in collisional radiative models have to take good equilibrium constant. That is to say these equilibrium constants have to be calculated taking external constraints and hypotheses on internal temperatures. This is usually not the case.

Furthermore, we have tested several approaches to determine the viscosity. If the plasma is out of thermal equilibrium, we have shown that if the plasma is highly ionized at low heavy species temperature Wilke formulation using Blottner coefficients cannot be used. Surprisingly, it is used in several calculation code of fluid dynamic without any comments. Comparing with Chapman Enskog methods, Gupta and al approach seems to give better results. So in a future work, we have to test the sensitivity of a fluid calculation code to transport coefficients. We have also to pursue the work by including a state to state model to determine the transport coefficients taking each quantum level into account.

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